[19]中华人民共和国专利局

[11] 公开号 CN 1083773A

[12] 发明专利申请公开说明书

[21]申请号 93117042.7

[51]Int.Cl[5]
B32B 5/18

[43]公开日 1994年3月16日

[22]申请日 93.8.28

[30]优先权

[32]92.8.28 [33]DE[31]P4228779.0

[32]93.5.27 [33]DE[31]P4317691.7

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B32B 9/04

说明书页数: 附图页数:

[54]发明名称 基于固化淀粉泡沫的生物降解叠层复合材料及其制造方法

[57]摘要

本发明提出基于固化淀粉泡沫的可生物降解叠层复合材料及其制造方法，在该制造过程中，淀粉泡沫同时与另一材料层结合。本发明的优点包括制造工艺简单，成本低并且制造的复合材料用途广。

权 利 要 求 书

1. 叠层复合材料，包括至少一层泡沫和至少另一材料层，其中泡沫材料为固化淀粉泡沫，并且各层间不加粘结剂而就地相互结合。

2. 权利要求 1 的复合材料，其中淀粉泡沫含天然淀粉。

3. 权利要求 1 或 2 的复合材料，其中淀粉泡沫含改性淀粉。

4. 权利要求 1—3 中任一项的复合材料，其中淀粉泡沫进行染色。

5. 权利要求 1—4 中任一项的复合材料，其中淀粉泡沫含纤维和/或填料。

6. 权利要求 1—5 中任一项的复合材料，其中另一层由纸，纸板，花纹板，天然和/或合成纤维，玻璃和/或陶瓷纤维制成的纺织品和/或混合织物，薄木片，皮革，人造皮，合成材料带，生物聚合物带和金属材料带，制造复合材料时就地形成的合成和/或生物聚合物材料薄膜以及上述材料的组合物制成。

7. 权利要求 1—6 中任一项的复合材料，其中另一层单面与淀粉泡沫接触。

8. 权利要求 1—7 中任一项的复合材料，其中另一层已印刷或可印刷。

9. 权利要求 1—8 中任一项的复合材料，其中另一层由多层构成。

10. 权利要求 9 中任一项的复合材料，其中淀汾泡沫位于各层之间

11. 权利要求 11—10 中任一项的复合材料，其中该复合材料制成具有空腔的板。

12. 权利要求 11 中的复合材料，其中在叠板之间板状空心区域压出空腔。

13. 尤其宜于包括糖果的包装材料，其中包括权利要求 1—12 中任一项所述的叠层复合材料。

14. 权利要求 1—12 中任一项所述的叠层复合材料的制造方法，其步骤包括：

a. 将淀粉悬浮液和至少另一材料引入模具中，

b. 使淀粉泡沫固化并同时与该另一材料结合而成叠层复合材料以及

c. 从模具中脱除该叠层复合材料。

15. 权利要求 14 的要求，其中模具在步骤 *a* 之前加热。

16. 权利要求 14 或 15 的方法，其中步骤 *a* 中加入淀粉水悬浮液。

17. 权利要求 14，15 或 16 的方法，其中步骤 *a* 中加入染色淀粉悬浮液。

18. 权利要求 14—17 中任一项的方法，其中步骤 a 中注入淀粉悬浮液。

19. 权利要求 14—18 中任一项的方法，其中步骤 a 中使淀粉悬浮液减压发泡。

20. 权利要求 14—19 中任一项的方法，其中步骤 a 中在加入淀粉悬浮液之前加入另一材料。

21. 权利要求 14—20 中任一项的方法，其中另一材料以液态和/或固态粉状 材料加入并在步骤 a 中成为薄层而与淀粉泡沫结合形成叠合复合材料。

22. 权利要求 14—21 中任一项的方法，其中另一材料先预成型后引入步骤 a。

23. 权利要求 22 的方法，其中另一材料预成型为壳体。

24. 权利要求 14—23 中任一项的方法，其中步骤 a 中加入包括 20—45%淀粉颗粒，0—10%膨胀淀粉和水的淀粉悬浮液，模具加热到 180—270℃，优选 200—250℃，并且在 30—90 秒，优选 45—75 秒后进行步骤 c。

25. 应用权利要求 1—12 中任一项所述的复合材料作为食品，尤其是巧克力包装容器的分隔装置，折迭盒或可避免运输损伤的软垫，冷冻食品的隔热包装以及冷热饮杯。

说　明　书

基于固化淀粉泡沫的生物降解叠层复合材料及其制造方法

本发 明涉及基于固化淀粉泡沫的生物降解叠层复合材料及其制造方法。

这种复合材料可用作包装材料如结构材料，用以例如隔冷，隔热或隔音或减震。

由聚苯乙烯制成的常见泡沫包装材料(*Styrofoam*)尤其是食品包装材料突出的问题是其废弃处理，因为这种塑料本身不会腐烂，只能在用完后循环。

在已知方法中，已用淀粉悬浮液代替塑料，其中液态组分一旦引入加热模具就会蒸发并使悬浮液发泡或膨胀，而该材料在模具中保持规定的膨胀时间以进行干燥和固化，这期间湿份逸出。然后脱模，放出泡沫块，这样生产的泡沫块会腐烂并可再循环，而且具有隔冷和隔热以及减震性，但缺点是若其重量不够或不是相当厚，则其强度相当低。此外，因其呈现多孔表面，尤其是难于在其表面上印刷，所以这种材料不能用于某些领域。

相比之下，本发明目的是提出可生物降解叠层复合材料，其特征是其强度高，制造方法简单，成本低并且用途广。

该目的可通过以下特征达到。

在达到该目的的过程中，本发明基于这样一种构思，即淀粉发泡和固化形 成泡沫层并同时将其与另一材料层结合得到叠层复合材料，其中这 另一叠层材料可结合到淀粉泡沫之中和/或紧贴泡沫一侧或两侧放置并作为支持体，载体或基体。

本发明具有以下优点。

淀粉可在不另加添加剂的情况下应用，并且可用各种材料与淀粉泡沫结合而制成叠层复合材料，尤其是根据这另一叠层材料的情况，可使制成的叠层复合材料易于印刷或染色。该叠层复合材料因固化淀粉泡沫的多孔性而可在机械力作用下稳定，并且显示出优异的隔音效果以及热和电绝缘性。此外，该叠层材料还可有效减震。本发明材料可最有效地用作糖果包装材料，因为该叠层复合材料上可印制广告并可具有糖果所要求的吸收冲击和隔热性。

以下详述本发明。

本发明叠层复合材料包括至少一层固化淀粉泡沫并结合至少另一层材料，从而形成叠层复合材料。而该另一材料优选为平面材料并优选单面覆盖淀粉泡沫。

本发明方法基于可含天然和/或改性淀粉的淀粉悬浮液，其中天然淀粉可为任何来源的天然或杂化物形态淀粉，并可用例如马铃薯，木薯，豌豆，蚕豆，玉米，*wax corn*，直链淀粉含量高的玉米，谷物如小麦及其部分制品，大麦或高粱，而改性淀粉为物理和/或化学改性生产的淀粉衍生物。优选用淀粉水悬浮液并可混入与食品相容的

染料。

而且，该方法所用的另一叠层材料优先选自纸，纸板，花纹板，纺织品，薄木片，皮革，人造皮，合成材料膜，生物聚合物膜和金属薄膜以及这些材料的组合物。该另一叠层材料优选为平面材料，这可由叠层复合材料如包装材料的最终形式确定并可以坯料或预制品形式引入模具中，而且这优选在淀粉悬浮液加入之前进行。

该淀粉悬浮液优选以确定量注入模具中，悬浮液在该加热模具中蒸发后发泡并填入空腔。在这期间以及在干燥和化学物理固化过程中，淀粉与另一叠层材料结合成为整体，然后从模具中脱出而得叠层复合材料。这些工艺操作可通过模具中的内压升高而加速并优选在控制压力和温度的情况下进行。

惊人的是，在适当地进行该方法时，相当高的模塑温度并不会影响该另一叠层材料，而且在引入模具和随后的变形之前，对于在该另一叠层材料，尤其是纸，纸板或花纹板上进行的任何印刷而言，也同样如此。尤其是如果将淀粉悬浮液单面涂到另一叠层材料，则在从模具中脱模时仅在该复合叠层材料一侧出现印刷图案。在单侧涂淀粉悬浮液时，循环花纹板材料可用来包装食品，其中该材料不会与包装材料外侧的食品接触。

为了得到几个可印刷或光滑的表面并提高强度，可将多层另一叠层材料送入模具中。在这种情况下，在该另一叠层材料层间引入淀粉悬浮液。

通过适当设计模具，可在叠层复合材料中形成开孔，空腔，网或带等结构，这从包装及强度角度看可能是有意义的。从模具中脱出后，该材料可通过变形，贴签，打印和/或编号。

该方法优选用来生产包装材料，在这种情况下所用另一叠层材料可预成型为包装壳体形状。

另一叠层材料和淀粉泡沫的组合可使最终制品具有的强度高于各单一组分或其未加粘结的加合物的强度。该叠层材料比重小，厚度很薄，而且其隔冷和隔热以及减震性均大大高于常见塑料，还可抗静电。

例如，平面材料和淀粉泡沫的组合不要求加添加剂如热或冷胶或塑料等，致使该叠层复合材料除了可生物降解并可制成堆肥而外，还易于循环，因为可作为单一材料排除，而且费用极低。尤其是用纸，纸板或花纹板作平面材料时，所得叠层复合材料可循环进入纸，纸板或花纹板生产过程中。

本发明叠层复合材料的性质可使其除了作包装材料而外，还可有多种用途，如用于建筑，电子和汽车制造业达到绝缘目的。此外，该材料还可用于具有高稳定性的装饰制品如家具，其中由于其寿命短，就必须可循环使用。

以下用实施例详述本发明。

在连续工艺中，制成淀粉悬浮液，其中液态和固态添加剂自动测量，在均化步骤中细分散并进行反应。马铃薯淀粉，玉米膨胀淀粉

和水在悬浮液中的重量比为100：5.2：106。

操作中将结构类似于对开式铁芯并包括由铸铁制成包装壳体形状的模具的温度和压力可控膨胀模塑装置加热到220℃，其中该模塑装置的模板由两部分制成，平面花纹板预成型壳体材料放在下面的模件上。然后将21.5g淀粉悬浮液倒入壳体中并将两部分模板扣紧，其中淀粉悬浮液发泡，干燥，固化并与花纹板壳体紧密结合。膨胀约70秒后，取出最终成型的包装壳体，为叠层复 合材料。该膨胀模塑装置可用来生产板状叠层复合材料的多层表面结构，其中仅需替换铸铁制成的模具而已。因此，可制成例如贮存各种不型零部件(如螺钉或小型家用制品) 或贮存压敏和易腐食品(如巧克力或鸡蛋)的容器的各种分隔装置。

壳体比重190kg/m^3，包装性能优异，其强度高，重量轻，并具有隔冷和隔热，减震和抗静电性能，而且易于生物降解和制成堆肥以及极易循环用于造纸业。

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CANADIAN INTELLECTUAL PROPERTY OFFICE

(12) (19) (CA) **Brevet-Patent**

(11) (21) (C) **2,143,432**
(86) 1993/08/27
(87) 1994/03/17
(45) 2000/11/28

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(51) Int.Cl.^{6} B32B 5/18
(30) 1992/08/28 (P 42 28 779.0) DE
(30) 1993/05/27 (P 43 17 691.7) DE

(54) **MATERIAU MIXTE LAMINE BIODEGRADABLE, A BASE DE MOUSSE D'AMIDON RETICULEE; METHODE DE PREPARATION**

(54) **BIODEGRADABLE LAMINATED COMPOSITE MATERIAL BASED ON CURED STARCH FOAM AND METHOD FOR PREPARING IT**

(57) There is provided biodegradable laminated composite material based on cured starch foam and a method for preparing it. During the preparation the starch foam is simultaneously combined with an additional layer of a further material. The advantages of the invention include the simple and cost-efficient method of preparation and the multiple applications of the composite material.

Abstract

Biodegradable Laminated Composite Material Based on Cured Starch Foam and Method for Preparing it

There is provided biodegradable laminated composite material based on cured starch foam and a method for preparing it. During the preparation the starch foam is simultaneously combined with an additional layer of a further material. The advantages of the invention include the simple and cost-efficient method of preparation and the multiple applications of the composite material.

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Biodegradable Laminated Composite Material Based on Cured Starch Foam and Method for Preparing it

The invention relates to biodegradable laminated composite material based on cured starch foam and a method for preparing it.

Such composite materials can be used as packaging materials, as construction materials, for example, for cold, heat or sound insulation, or for shock absorption.

Conventional foam packaging materials made of polystyrene (Styrofoam), especially for food stuff, are problematic in particular in terms of their disposal. Such plastics virtually do not rot and can only be recycled after sorting.

In a known method a starch suspension is used in place of plastics. Liquid parts, once introduced in a heated die, evaporate and cause the suspension to foam or expand. The material remains in the mold over a particular dwell time for drying and curing while moisture escapes. Then the mold is released and the foam part ejected. Foam parts thus produced rot and are recyclable. Furthermore, they show cold- and heat-insulating as well as shock-absorbing properties. However, they have the drawback of exhibiting relatively low strength unless they are heavyweight or have fairly thick walls. Furthermore, they are not useful for

certain applications due to their porous surfaces, in particular it is difficult to print on them.

By contrast, the object underlying the present invention is to provide biodegradable laminated composite material characterized by high strength, a simple and cost-efficient method of preparation and multiple applications.

This object is achieved by providing the features indicated in the claims.

In achieving the object, the invention is based on the concept of foaming and curing starch to form a layer and simultaneously combining it with an additional layer of a further laminate material to obtain laminated composite material. Said further laminate material can be integrated into the starch foam and/or positioned adjacent to the foam uni- or bilaterally and serves as support, carrier or substrate.

The invention has the following advantages.

Starch can be used without further additives. A variety of materials can be combined with the starch foam to form laminated composite material. In particular, the laminated composite material, on account of said further laminate material, is easy to print on or dye. The laminated composite material is mechanically stable and exhibits excellent sound, temperature and electrical insulation properties due to the porosity of the cured starch foam. Furthermore, it is effective in absorbing shock. The invention can most advantageously be used as packaging material for sweets because the laminated composite material permits printing for publicity purposes and ensures shock absorption and heat insulation required for sweets.

The invention is further illustrated below.

The laminated composite material of the invention comprises at least a layer of cured starch foam combined with at least one further material to form laminated composite material. Preferably, said further material is flat material covered with starch foam preferably unilaterally.

The method of the invention is based on a starch suspension which may contain native and/or modified starch. The native starch may be of any origin in natural or hybrid form and derived, for example, from potatoes, manioc, rice, corn, wax corn, corn with high amylose content, grain such as wheat and fractions prepared therefrom, barley or sorghum. The modified starch is a physically and/or chemically produced starch derivative. Preferred are aqueous starch suspensions that may be mixed with dyes compatible with food stuff.

Furthermore, further laminate material is used in the method, which material preferably comprises paper, paperboard, cardboard, textiles, wood veneer, leather, imitation leather, films from synthetic, biopolymeric and metallic materials as well as combinations of the aforementioned materials. Preferably, said further laminate material is flat material. It is determined by the final form of the laminated composite material, such as packages, and can be introduced in the mold either as a blank or in preformed state. This preferably occurs shortly before the starch suspension is added.

The starch suspension is preferably introduced in the die by injection and in measured amounts. In the heated mold the suspension foams following evaporation and fills the cavities. During that time and during the drying and chemicophysical curing processes the starch is combined with the further laminate material to form a unit that is subsequently released from the mold as laminated composite material. These processes are promoted by the increased

internal pressure in the die and preferably conducted while controlling pressure and temperature.

It is surprising that the relatively high molding temperature does not affect the further laminate material when the method is conducted properly. This also applies for any printing done to the further laminate material, especially paper, paperboard or cardboard, prior to introduction in the die and subsequent deformation. In particular, if the starch suspension is applied to the further laminate material unilaterally, the print appears on one side of the laminated composite material upon release from the mold. In the case of unilateral application of the starch suspension, recycled cardboard material can be used for packaging food stuff which material does not come into contact with the food stuff at the outside of the packages.

To obtain several printable or smooth surfaces and to enhance strength, a plurality of layers of the further laminate material can be introduced in the die. In this case the starch suspension is mainly introduced between the layers of said further laminate material.

By proper design of the die, structures can be molded into the laminated composite material, such as, e.g., openings, cavities, webs or ribs. This might make sense for packaging and strength reasons. After removal from the die, the material can be further processed by deforming, stamping, punching and/or formating.

A preferred application of the method is the production of packaging material. In this case the further laminate material can be preformed to a packaging shell.

The combination of further laminate material and starch foam results in the finished articles having much higher strength than its individual components or addition thereof without

intimate bonding. The laminated composite material has low specific weight and relatively thin walls. Moreover, it exhibits considerably improved cold- and heat-insulating as well as shock-absorbing properties in comparison to conventional plastics and is antistatic.

The combination of, for instance, flat material and starch foam requires no additives such as hot or cold glue or plastics, etc. As a result, the laminated composite material can be easily recycled in addition to being biodegradable and compostable because it can be disposed of as monomaterial and at very low cost. In particular, if paper, cardboard or paperboard is used as the flat material, the laminated composite material can be recycled in the paper, cardboard or paperboard production.

The properties of the laminated composite material of the invention permit a multitude of applications other than packaging. For example, the material can be used in construction, electronics and the automobile manufacture for insulation purposes. Furthermore, it can be used for fashion articles having fairly high stability, such as furniture which must be recyclable due to their short life.

Using an example, the method of the invention will be described in more detail below.

In a continuous process a starch suspension is prepared wherein liquid and solid adjuvants are automatically measured, finely dispersed in a homogenization step and reacted. Potato starch, corn swelling starch and water are present in the suspension in a weight ratio of 100:5.2:106.

Furthermore, a temperature- and pressure-controlled expansion molding apparatus having a similar construction as a waffle iron and comprising a mold made of cast iron in the form of a packaging shell is heated to 220°C. The die of the

molding apparatus is made of two parts. A preformed shell is placed as flat cardboard material in the lower mold part. Then 21.5 g of starch suspension is poured into the shell and the two-part die is closed. The starch suspension is foamed, dried, cured and thereby solidly combined with the cardboard shell. After a dwell time of about 70 seconds, the finished packaging shell in the form of laminated composite material is removed.

The expansion molding apparatus can be rearranged for the production of a multitude of surface structures for plate-like laminated composite materials. This merely requires replacement of the mold made of cast iron. Thus, a variety of sorting devices for containers to store assortments of small parts (e.g., screws or small household articles) or to store pressure-sensitive and perishable food stuff (e.g., chocolates or eggs) can be produced, for example.

The shell has a specific weight of 190 kg/m^3 and excellent packaging properties. It combines high strength and low weight, exhibits cold- and heat-insulating, shock-absorbing and antistatic properties. It is readily biodegradable and compostable as well as excellently recyclable in the paper industry.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. Laminated composite material comprising at least a foam layer and at least one additional layer of a material characterized in that the foam material is cured starch foam and the layers are biodegradable and interconnected in situ without a coupling agent.

2. Composite material as defined in Claim 1 characterized in that the starch foam contains native starch.

3. Composite material as defined in any of Claims 1 and 2 characterized in that the starch foam contains modified starch.

4. Composite material as defined in any of Claims 1 to 3 characterized in that the starch foam is dyed.

5. Composite material as defined in any of Claims 1 to 4 characterized in that the starch foam contains fibers and/or fillers.

6. Composite material as defined in any of Claims 1 to 5 characterized in that the additional layer is made of paper, paperboard, cardboard, textiles from natural and/or synthetic fibers and/or mixed fabrics, wood veneer, leather, sheets from synthetic and biopolymeric materials, films from synthetic and/or biopolymeric materials that are produced in situ in the preparation of the composite material, as well as combinations of the aforementioned materials.

7. Composite material as defined in any of Claims 1 to 6 characterized in that the additional layer is combined with the starch foam unilaterally.

8. Composite material as defined in any of claims 1 to 7 characterized in that the additional layer is or can be printed on.

9. Composite material as defined in any of claims 1 to 8 characterized in that the additional layer is composed of a plurality of layers.

10. Composite material as defined in claim 9 characterized in that the starch foam is positioned between the plurality of layers.

11. Composite material as defined in any of claims 1 to 10 characterized in that it is formed to a plate having cavities.

12. Composite material as defined in claim 11 characterized in that the cavities pressed in the plate form hollow spaces between stacked plates.

13. Packaging material comprising the laminated composite material as defined in any of claims 1 to 12 especially for use in packages for sweets.

14. A method for preparing laminated composite material as defined in any of claims 1 to 12 comprising the steps of:

a. introducing a starch suspension and at least one further laminate material in a die,
b. curing the starch foam and simultaneously combining it with said further material to form laminated composite material, and
c. removing said laminated composite material from the mold.

15. A method as defined in claim 14 characterized in that the die is heated prior to step a.

16. A method as defined in claim 14 or 15 characterized in that an aqueous starch suspension is added in step a.

17. A method as defined in claim 14, 15 or 16 characterized in that a dyed starch suspension is added in step a.

18. A method as defined in any of claims 14 to 17 characterized in that the starch suspension is injected in step a.

19. A method as defined in any of claims 14 to 18 characterized in that the starch suspension is pressure-foamed in step a.

20. A method as defined in any of claims 14 to 19 characterized in that the further material is added prior to the starch suspension in step a.

21. A method as defined in any of claims 14 to 20 characterized in that the further material is added as liquid and/or solid, powdery material and a layer is produced in step a, which layer combined with the starch foam forms the laminated composite material.

22. A method as defined in any of claims 14 to 21 characterized in that the further material is first preformed and then introduced in step a.

23. A method as defined in claim 22 characterized in that the further material is preformed to a shell.

24. A method as defined in any of claims 14 to 23 characterized in that a starch suspension comprising 20-45% of granular starch, 0-10% of swelling starch and water is added in step a, wherein the die is heated to a temperature of 180-270°C, preferably 200-250°C, and step c is taken after 30-90 seconds, preferably 45-75 seconds.

25. Use of the composite material as defined in any of claims 1 to 12 as sorting devices for containers for packaging goods, in particular chocolates, as foldable boxes or as padding to avoid transportation damage, as heat insulation packaging for frozen products or as cups for cold and hot drinks.